CHAPTER

NINE

REACTIONS IN SOLUTION

Chemical reactions are most often conducted in the liquid phase, and most studies of reaction mechanisms in organic and inorganic systems concern solution reactions. That has been true to the present time despite the potentially greater depth of theoretical understanding of gas-phase processes.

The present chapter considers a number of issues that have to do with reactions in solution. Some are of a theoretical nature concerning the diffusion rates of solutes and applications of activated complex theory to questions of solvent effects and reactivity; others are of a more practical bent dealing with salt effects of inert electrolytes and rate changes at very high pressures.

9-1 THE NATURE OF REACTIONS IN A SOLVENT

Relatively few reactions are amenable to study in both the gas phase and a variety of solvents. Among them is the decomposition of N_2O_5:

$$N_2O_5 = 2NO_2 + \tfrac{1}{2}O_2 \tag{9-1}$$

The formation of tetraethylammonium iodide, although not a suitable gas-phase reaction, can be conducted in many polar solvents:

$$Et_3N + EtI = Et_4N^+I^- \tag{9-2}$$

Kinetic data for reactions (9-1) and (9-2) are summarized in Table 9-1. On the one hand, the rate of N_2O_5 decomposition can be seen to be the same in the gas phase

Table 9-1 Solvent effects on reaction rates

Reaction (9-1): $N_2O_5 = 2NO_2 + \frac{1}{2}O_2$

Solvent	$10^5\ k_{298}/s^{-1}$	$\log_{10} A$	E_a/kJ mol^{-1}
Gas phase	3.4	13.6	103
CCl_4	4.1	13.8	107
$CHCl_3$	3.7	13.6	103
$C_2H_2Cl_2$	4.8	13.6	102
C_2HCl_5	4.3	14.0	105
CH_3NO_2	3.1	13.5	102
Br_2	4.3	13.3	103
$N_2O_4(l)$	7.1	14.2	105
$HNO_3(l)$	0.15	14.8	118

Reaction (9-2): $Et_3N + EtI = Et_4N^+I^-$

Solvent	Dielectric constant, ϵ	$10^5\ k_{373}/M^{-1}\ s^{-1}$	$\log_{10} A$	E_a/kJ mol^{-1}
n-Hexane	1.9	0.5	4.0	67
Toluene	2.40	25.3	4.0	77
Benzene	2.23	39.8	3.3	48
p-Dichlorobenzene	2.86	70	4.5	53
m-Dichlorobenzene	4.9	111	–	–
Fluorobenzene	5.4	116	3.9	48.9
Bromobenzene	–	166	4.6	52.3
o-Dichlorobenzene	9.9	250	5.1	54.4
Acetone	21.4	265	4.4	49.8
Benzonitrile	25.2	1120	5.0	49.8
Nitrobenzene	36.1	1380	4.9	48.5

as in solution and nearly invariant from one solvent to the next. On the other hand, reaction (9-2) is quite sensitive to changes in solvent; it is faster the more polar the solvent. (A quantitative treatment will be given in Sec. 9-4.) The latter reaction, considering its nature, would be likely to have a polar transition state, and it would be expected to be stabilized in solvents of high dielectric constant. These data serve to show that no single simple generalization can be drawn: In some cases there may be reactions which proceed seemingly independently of solvent, but in general that will not be the case.

It has been pointed out[1] that the mean distance between two solutes at 0.02 mol/dm^3 concentration is roughly the same as in the gas phase at one atmosphere pressure, the separation being ~10 molecular diameters. Formation of such an aqueous solution, in which the solvent:solute ratio will be ca. $10^3:1$, will necessarily reduce the mean free paths of the reactants to the order of one molecular diameter.

Rather than collisions between noninteracting partners, as in the gas phase, solutes in solution tend to undergo multiple collisions within a solvent cage; this event is referred to as an "encounter."

9-2 THE RATES OF DIFFUSION-CONTROLLED REACTIONS

The maximum rate at which two solutes can react is controlled by the relative rate of diffusion or, more precisely, the encounter rate of the solutes. The mathematical model will have the same significance for solution reactions as collision theory has for gaseous reactants, although the mathematical formulation is rather different. A simple approach[2,3] involving Fick's laws of diffusion will be given, although more rigorous formulations are possible.[4]

The quantity of solute B crossing a plane of area A in unit time (1 s) is a flux designated by J or dn_B/dt, and it has the units molecules s^{-1}. Fick's first law states that this flux is inversely proportional to the gradient in concentration with distance and is, of course, negative, since the flow will be in a direction to offset the gradient:

$$J = \frac{dn_B}{dt} = -DA\frac{dc}{dx} \tag{9-3}$$

where the proportionality constant D is called the diffusion constant. A typical solute has $D \approx 1 \times 10^{-9}$ m^2 s^{-1}, and in practice, values do not vary greatly either with solute or with solvent for solvents of ordinary viscosity.

Consider the bimolecular reaction of solutes A and B, assumed to be uniformly distributed throughout the solution. The concentration of B is depleted near the still unreacted A by virtue of the rapid reaction of A and B, which creates a concentration gradient. It is assumed that there is a critical distance r_{AB}, approximately the sum of molecular radii $r_A + r_B$, at which reaction occurs. At distances $r \leqslant r_{AB}$, $[B] = 0$; beyond this distance $[B] = [B]^0$ at $r > r_{AB}$, where $[B]^0$ symbolizes the bulk concentration of B at $r = \infty$.

Provided the bulk concentrations remain constant, the flux J of Eq. (9-3) is also constant. It is assumed that there is a spherical distribution of potential reactants (B) around a particular molecule of A and that the distance r is measured from A. The surface area of a sphere a distance r from A is $4\pi r^2$, and the expression for the flow of B toward A is

$$J = -D_{AB}(4\pi r^2)\frac{d[B]}{dr} \tag{9-4}$$

where D_{AB} represents the diffusion coefficient for relative diffusion of reactive molecules.

Integration of Eq. (9-4) between the indicated limits affords this result:

$$J\int_{r_{AB}}^{\infty} \frac{dr}{r^2} = -4\pi D_{AB}\int_0^{[B]^0} d[B] \tag{9-5}$$

$$\frac{J}{r_{AB}} = -4\pi D_{AB}[B]^0 \tag{9-6}$$

The rate of this bimolecular reaction is given by $-d[A]/dt = k_{obs}[A][B]^0$, but that is also equal to the flux of B toward A, $-J$, multiplied by [A], or $-d[A]/dt = -J[A]$.

Substitution of Eq. (9-6) into these relations gives

$$k_{\text{obs}} = \frac{-d[\text{A}]/dt}{[\text{A}][\text{B}]^0} = \frac{-J[\text{A}]}{[\text{A}][\text{B}]^0} \tag{9-7}$$

$$k_{\text{obs}} = 4\pi r_{\text{AB}} D_{\text{AB}} \tag{9-8}$$

on a molecular basis, or

$$k = 4\pi N r_{\text{AB}} D_{\text{AB}} \tag{9-9}$$

on a molar basis. This latter relation is sometimes referred to as the Smoluchowski equation. Substituting typical values, $r_{\text{AB}} = 4 \times 10^{-10}$ m and $D_{\text{AB}} = 2 \times 10^{-9}$ m^2 s^{-1},

$$k = 4\pi \times 6 \times 10^{23} \, \frac{\text{molecules}}{\text{mol}} \times 4 \times 10^{-10} \, \frac{\text{m}}{\text{molecule}} \times 2 \times 10^{-9} \, \frac{\text{m}^2}{s} \times \frac{10^3 \text{ dm}^3}{\text{m}^3}$$

$$k = 6 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

This value, often taken as ca. 10^{10} M^{-1} s^{-1}, is referred to as the diffusion-controlled rate constant. It is some 30 times lower than the calculated value of the comparable parameter for gas-phase collision rates, Z'_{AB}.

For interacting particles (ions or dipoles) an additional factor must be incorporated into Eq. (9-9) to account for attractive or repulsive forces, which gives

$$k = 4\pi DN \frac{N z_{\text{A}} z_{\text{A}}}{\epsilon RT} \, \frac{1}{\exp(z_{\text{A}} z_{\text{A}} N/\epsilon RT \sigma_{\text{AB}}) - 1} \tag{9-10a}$$

This equation, for oppositely charged ions, becomes

$$k \simeq 4\pi DN \frac{N z_{\text{A}} z_{\text{B}}}{\epsilon RT} \tag{9-10b}$$

where the z's are the ionic charges and ϵ is the dielectric constant of the solvent. For water at 298 K the ratio as a function of $z_{\text{A}} z_{\text{B}}$ and σ_{AB} is as shown in Table 9-2.

This calculation places an approximate upper limit, roughly 10^{10} dm^3 mol^{-1} s^{-1}, on the rate constant for a bimolecular reaction in solution. Reactions of the hydrated

Table 9-2 Influence of ionic charge on the diffusion-controlled rates of second-order reactions

Entries are $k_{\text{ions}}/k_{\text{molecules}}$

	$10^{10}\,\sigma_{\text{AB}}/\text{m}$		
$z_{\text{A}} z_{\text{B}}$	2.00	5.00	10.0
+2	0.005	0.17	0.45
+1	0.10	0.45	0.69
−1	3.7	1.9	1.4
−2	7.1	3.0	1.9

proton, a species having an unusually high diffusion constant, can exceed that value. For example, the reaction $H^+(aq) + OH^- \longrightarrow H_2O$ has $k = 1.4 \times 10^{11}$ dm^3 mol^{-1} s^{-1}, probably the highest value known. Because of the limitation, it is sometimes possible to make a distinction between alternatives which would normally be impossible from kinetics. An illustration of this consideration in distinguishing between alternative mechanisms was given in Sec. 5-3.

9-3 APPLICATIONS OF ACTIVATED COMPLEX THEORY

The basic formulation developed in Chap. 8 for gas-phase reactions is written

$$k_{\text{gas}} = \frac{RT}{Nh} K^{\ddagger} \tag{9-11}$$

Effects due to, say, changes in solvent or solvent composition or ionic strength arise from changes in activity coefficients, a situation which does not assume major importance in gases.

The general method for handling such cases will be given here, and applications will be given in subsequent sections. The value of $K^{\ddagger}$ can be written in terms of activities a and related to that containing concentrations by appropriate activity coefficients. It is

$$K^{\ddagger}_{\text{actual}} = \frac{a^{\ddagger}}{a_A a_B} = \frac{[(AB)^{\ddagger}]}{[A][B]} \times \frac{\gamma^{\ddagger}}{\gamma_A \gamma_B}$$

Substitution into (9-11), with the reference state being an ideal solution ($\gamma^{\ddagger} = \gamma_A = \gamma_B = 1$), yields

$$k_{\text{actual}} = k_{\text{ref}} \frac{\gamma_A \gamma_B}{\gamma^{\ddagger}} \tag{9-12}$$

This relation, the Brønsted-Bjerrum equation, is the basis for considering salt effects and solvent effects. The key assumption in its derivation is that the reaction rate is proportional to the *concentration* of the activated complex, $[(AB)^{\ddagger}]$, and not to its activity.

9-4 SOLVENT EFFECTS ON POLAR AND IONIC REACTIONS

We can consider three cases for a second-order reaction: two polar molecules, two ions, and one of each.

Kirkwood[5] gives expressions for the free energy of transfer of a polar molecule (of dipole moment μ and radius r) from a medium of unit dielectric constant to one having a value ϵ:

$$\Delta G = \frac{-N\mu^2}{r^3} \frac{\epsilon - 1}{2\epsilon + 1} \tag{9-13}$$

The value of the rate constant according to Eq. (9-12) becomes

$$k_{\text{actual}} = k_{\text{ref}} \exp\left(\frac{N}{RT}\right)\frac{\epsilon - 1}{2\epsilon + 1}\left(\frac{\mu_{\ddagger}^2}{r_{\ddagger}^3} - \frac{\mu_A^2}{r_A^3} - \frac{\mu_B^2}{r_B^3}\right) \tag{9-14}$$

where k_{ref} refers to the state with $\epsilon = 1$ (as in the gas phase). The data given in Table 9-1 for reaction (9-2) are shown in Fig. 9-1 in a plot of log k versus $(\epsilon - 1)/(2\epsilon + 1)$ in accord with relation (9-14) provided the μ^2/r^3 terms are solvent-independent. Perhaps we should limit our interpretation to one qualitative matter. The positive slope of Fig. 9-1 is consistent with development of ionic charge in the activated complex for which one would predict a large value of $\mu_{\ddagger}$ and a small value of $r_{\ddagger}$. It can also be shown (Prob. 9-1) that a linear variation of ln k with $1/\epsilon$ is expected to a reasonable accuracy.

An electrostatic expression[5] for the free energy of transfer of two ions of charges z_A and z_B from infinite separation to their reaction distance is

$$\Delta G_{\text{el}}^{\ddagger} = \frac{N z_A z_B e^2}{\epsilon r_{\ddagger}} \tag{9-15}$$

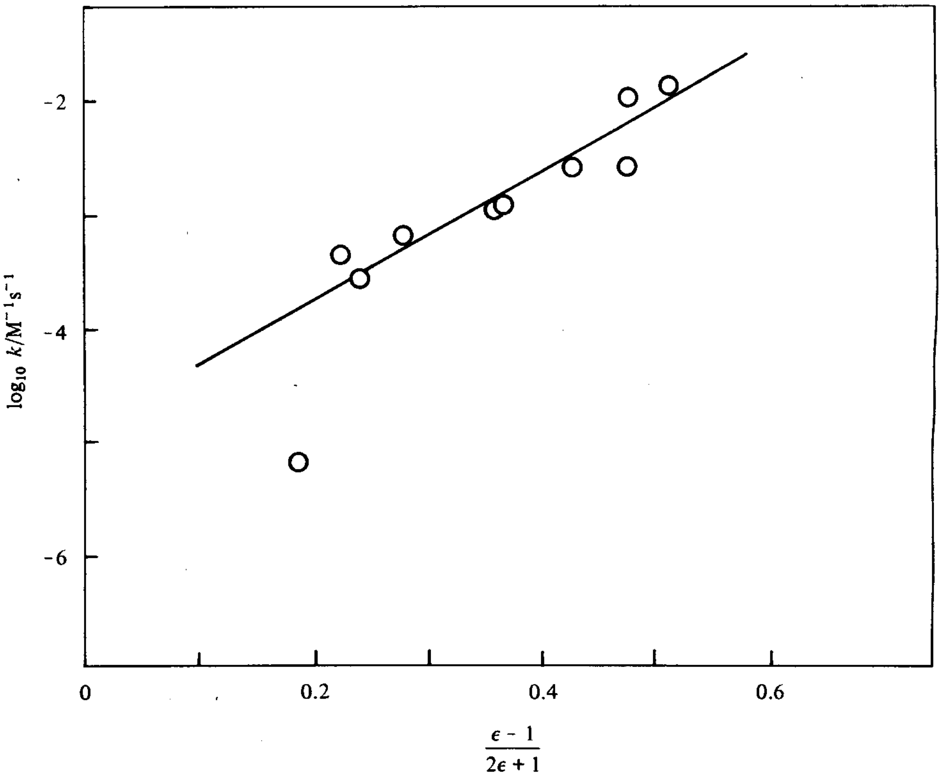

Figure 9-1 Plot of $\log_{10} k$ versus $\epsilon - 1/2\epsilon + 1$ for reaction 9-2. See Eq. (9-14) and Table 9-1.

The same procedure results in the expression

$$k_{\text{actual}} = k_{\text{ref}} \exp\left(\frac{-Nz_A z_B e^2}{\epsilon RTr_\ddagger}\right) \tag{9-16}$$

where the reference state has $\epsilon = \infty$. A linear variation of $\ln k$ with $1/\epsilon$ is predicted.

A similar treatment for reaction of an ion and a polar molecule gives

$$k_{\text{actual}} = k_{\text{ref}} \exp\left(\frac{Nz^2 e^2}{2\epsilon RT}\right)\left(\frac{1}{r_{\text{ion}}} - \frac{1}{r_\ddagger}\right) \tag{9-17}$$

Thus in all three cases examined, the variation of rate constant with dielectric constant is given by the linear plot of $\ln k$ versus $1/\epsilon$.

9-5 SALT EFFECTS ON SECOND-ORDER IONIC REACTIONS

The equation of Debye and Hückel for the activity coefficient of an ion of charge z_i is†

$$\log_{10} \gamma_i = \frac{-Az_i^2 \mu^{1/2}}{1 + \mu^{1/2}} \tag{9-18}$$

where μ is the ionic strength of the solution ($\mu = \frac{1}{2}\Sigma[\text{i}]\, z_i^2$, the sum being made for all ions present) and A is a collection of physical constants with the value 0.509 for water at 298 K. (Values in water at other temperatures are tabulated.[8])

Substitution of Eq. (9-18) into (9-12), noting that $z^\ddagger = z_A + z_B$, yields for a reaction following second-order kinetics

$$\log k = \log k_{\text{ref}} + \frac{A(z_A + z_B)^2 \mu^{1/2}}{1 + \mu^{1/2}} - \frac{Az_A^2 \mu^{1/2}}{1 + \mu^{1/2}} - \frac{Az_B^2 \mu^{1/2}}{1 + \mu^{1/2}} \tag{9-19}$$

$$\log k = \log k_{\text{ref}} + 2z_A z_B \frac{A\mu^{1/2}}{1 + \mu^{1/2}} \tag{9-20}$$

Taking the reference state as pure water, $\mu = 0$, Eq. (9-20) predicts that a plot of $\log k$ versus $2A\mu^{1/2}/(1 + \mu^{1/2})$ should have a slope given as the product of ionic charges on the reactants. Thus the rate of a second-order reaction between two cations or two anions should increase with increasing ionic strength, whereas the rate of a reaction between oppositely charged ions should decrease.

The validity of Eq. (9-20) has been proved numerous times, but one must not

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†Other forms of Eq. (9-18) are sometimes given. One is the so-called Debye-Hückel "limiting law,"

$$\log_{10} \gamma_i = -Az_i^2 \mu^{1/2} \tag{9-18a}$$

which is valid only at low ionic strength. Other forms with a nonunity coefficient of $\mu^{1/2}$ in the denominator and/or an added term linear in μ are sometimes used. For our purposes (9-18) or often even (9-18*a*) will suffice, although the reader should consult detailed references[6,7] as needed. The nonunity coefficient can be written as βa_i, where a_i is the distance of closest approach of the two ions and β a physical constant (in water 0.33×10^{-10} m^{-1}). In view of the limitations of the theory it is doubtful whether great significance can be attributed to a distance a_i so calculated.

expect it to be any more accurate than the Debye-Hückel relation itself. It cannot, therefore, be applied at high ionic strength, especially if the reactants bear high ionic charges.

Some authors object to the use of Eq. (9-18) in the form given. Their reason is that it contains a quantity, the single-ion activity coefficient, which cannot be measured directly. Identical results are obtained if the activity coefficients are expressed in terms of the values for salts. The derivations, however, are not given here.[9]

Little new information is gleaned from a study of salt effects in the dilute solution range in a study involving properly characterized reactants. The magnitude of the effect is based entirely upon the ionic charges, which are known in most instances. One use of salt effect studies has, in fact, been to determine or confirm the ionic charge of one reactant. Both $e^-(aq)$[10] and $Cu^+(aq)$[11] have been examined from that point of view, as have certain metalloproteins.[12] An illustration of the principles can be made by using published data[11] on the reaction of Cu^+ and $Co(NH_3)_5Cl^{2+}$. Table 9-3 summarizes the kinetic data on the reaction. Figure 9-2 depicts the variation of log k with $\mu^{1/2}$ [Eq. (9-18a)] and with $\mu^{1/2}/(1+\mu^{1/2})$ [Eq. (9-18)]. The slope shown for the linear portion at low ionic strength is the theoretical value (2.04) for a second-order reaction between ions of charge 1+ and 2+.

One must make allowance for salt effects when studying the kinetics of a reaction in which the reactants are ions. Imagine, for example, that the following reaction was studied with these starting concentrations: 2.00×10^{-3} M $[Co(NH_3)_5OH_2](ClO_4)_3$ and 6.00×10^{-3} M HCl.

$$Co(NH_3)_5OH_2^{3+} + Cl^- \longrightarrow Co(NH_3)_5Cl^{2+} + H_2O$$

The ionic strength of the starting solution would be 0.018 mol dm^{-3}, whereas that at the end, assuming the reaction went to completion, would be 0.010 mol dm^{-3}. The second-order rate constant for the reaction would increase steadily throughout the run owing to the change in μ. According to Eq. (9-20), the increase would amount to 12 percent (i.e., the value of k near completion would be some 1.12 times that mea-

Table 9-3 Ionic strength effects on the reaction[a] of $Cu^+(aq)$ and $Co(NH_3)_5Cl^{2+}$

Ionic strength μ/M	10^{-4} k/M^{-1} s^{-1}	$\mu^{1/2}$	$\dfrac{\mu^{1/2}}{1+\mu^{1/2}}$
9.4×10^{-4}	1.50	0.0307	0.0297
4.23×10^{-3}	1.84	0.065	0.061
9.8×10^{-3}	2.21	0.099	0.090
2.25×10^{-2}	2.86	0.150	0.130
3.98×10^{-2}	2.81	0.199	0.166
6.25×10^{-2}	4.08	0.250	0.200
1.00×10^{-1}	3.79	0.316	0.240
2.00×10^{-1}	4.98	0.447	0.309
1.00	7.60	1.00	0.500
3.00	11.3	1.73	0.634

[a] At 25.0°C; data from Ref. 11.

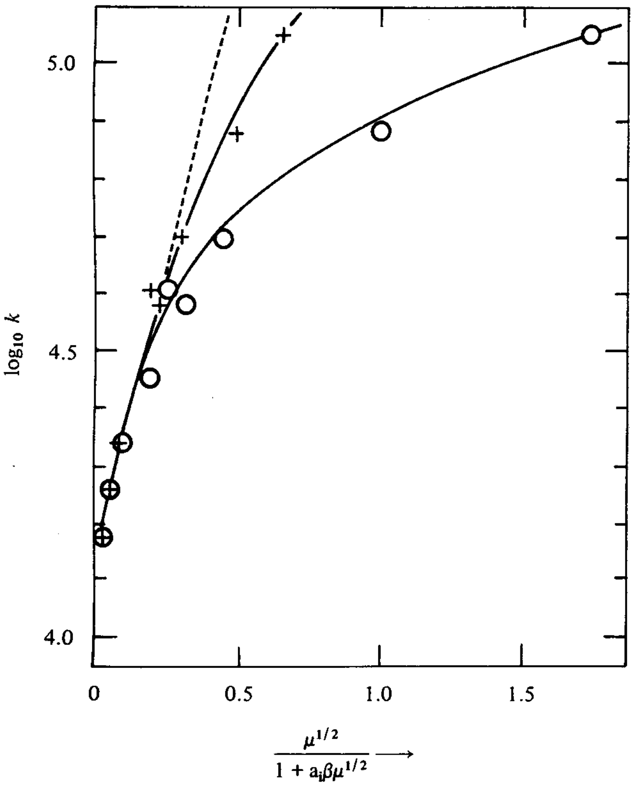

Figure 9-2 Plot of log k for the reaction of $Cu^+(aq)$ with $Co(NH_3)_5Cl^{2+}$ (data from Table 9-3 and Ref. 11). The abscissa represents either $\mu^{1/2}$ [circles, Eq. (9-18*a*), $a_i\beta = 0$] or $\mu^{1/2}/(1 + \mu^{1/2})$ [crosses, Eq. (9-18*a*), $a_i\beta = 1.00$]. The slope of the linear portion at low ionic strength is the theorectical value for this reaction, $2Az_Az_B = 2.04$.

sured initially). Worse yet, still greater discrepancies would be found from run to run employing different initial concentrations of the reactants.

The problem is usually circumvented by adding "inert" electrolytes to maintain constant ionic strength between runs. In this instance, for example, one might add perchloric acid, perchlorate ion being largely noncomplexing in water, such that each run had an ionic strength of, say, 0.500 mol dm^{-3}. Thus in the first experiment 0.482 M $HClO_4$ would be added. The final ionic strength would be 0.492 M, which means that k would increase only an insignificant 0.9 percent throughout the run [assuming Eq. (9-20) remains valid at the higher ionic strength]. Moreover, by adjusting the perchloric acid concentration so that each run has $\mu = 0.500$ mol dm^{-3}, values of k from experiments at different reactant concentrations should agree, provided the rate is independent of $[H^+]$. This notion, known as the *constant ionic strength principle*, is not exact in that individual electrolytes do not have identical activity coefficients at the same concentration, particularly at higher ionic strengths where specific interactions may become more important. It is a difficult problem to decide whether a small but systematic variation of the rate constant with reagent concentration is due to the growing importance of a new and genuine reaction pathway or to a medium effect arising from failure of the constant ionic strength principle over a wide range of concentrations.

9-6 SALT EFFECTS ON OTHER REACTION ORDERS

Consideration of the ionic strength dependence of a rate constant of other than second-order form is in order. A first-order reaction will show negligible salt effects because reactant and activated complex bear the same ionic charge; the same thing is true of a second-order reaction in which one component is a neutral molecule, including solvent.[†]

The question of the general expression for salt effects can best be considered by use of examples. Consider the reaction of Fe(III) and Sn(II) in $HClO_4/HCl$ solutions in which the major species are $Fe^{3+}(aq)$ and $Sn^{2+}(aq)$. The kinetic expression contains these terms:

$$\frac{-d[\mathrm{Fe^{3+}}]}{dt} = k_1 \frac{[\mathrm{Fe^{3+}}][\mathrm{Sn^{2+}}]}{[\mathrm{H^+}]} + k_2[\mathrm{Fe^{3+}}][\mathrm{Sn^{2+}}][\mathrm{Cl^-}] \tag{9-21}$$

Both k_1 and k_2 should show an appreciable salt effect, and we shall endeavor to develop a general method. One defines a *net activation process*[13] as a hypothetical reaction in which the activated complex is formed directly from the predominant forms of the reactants. For the two terms in the rate law given, the net activation reactions are

$$\mathrm{Fe^{3+} + Sn^{2+} + H_2O} \overset{K_1^\ddagger}{=\!=\!=} [\mathrm{FeSnOH^{4+}}]^\ddagger + \mathrm{H^+} \qquad (\Delta z_1^2)^\ddagger = 4 \tag{9-22}$$

$$\mathrm{Fe^{3+} + Sn^{2+} + Cl^-} \overset{K_2^\ddagger}{=\!=\!=} [\mathrm{FeSnCl^{4+}}]^\ddagger \qquad (\Delta z_2^2)^\ddagger = 2 \tag{9-23}$$

By the Debye-Hückel equation, the concentration of each activated complex (and therefore the rate) will vary with ionic strength in proportion to the values of the hypothetical constants $K_1^\ddagger$ and $K_2^\ddagger$.

The salt effects on k_1 and k_2 take the forms

$$\log k_1 = \log k_1^\circ + \log \frac{\gamma_{\mathrm{Fe^{3+}}}\gamma_{\mathrm{Sn^{2+}}}}{\gamma_{\mathrm{H^+}}\gamma_\ddagger}$$

$$\log k_1 = \log k_1^\circ + \frac{4A\mu^{1/2}}{1+\mu^{1/2}} \tag{9-24}$$

$$\log k_2 = \log k_2^\circ + \log \frac{\gamma_{\mathrm{Fe^{3+}}}\gamma_{\mathrm{Sn^{2+}}}\gamma_{\mathrm{Cl^-}}}{\gamma_\ddagger} \tag{9-25}$$

[†] Actually, neutral molecules have activity coefficients which are linear functions of ionic strength. The magnitude is much smaller than for ions, however, and it can be neglected in the present context.

$$\log k_2 = \log k_2^\circ + \frac{2A\mu^{1/2}}{1+\mu^{1/2}} \qquad (9\text{-}26)$$

The magnitude of the salt effect is given by the value and sign of the coefficient of the quantity $A\mu^{1/2}/(1+\mu^{1/2})$. The value for k_1 is 4 [Eq. (9-24)], and for k_2 it is 2 [Eq. (9-26)]. Those are just the respective values of $(\Delta z^2)^\ddagger$ shown for the net activation reactions of Eqs. (9-22) and (9-23), and that can be shown to be a general result. For the general situation in which the net activation process is

$$A^{z_A} + B^{z_B} + C^{z_C} + \cdots = (X^{z_X})^\ddagger + Y^{z_Y} + \cdots$$

$$\log k = \log k^\circ + \log \frac{\gamma_A\gamma_B\gamma_C\cdots}{\gamma_\ddagger\gamma_Y\cdots} \qquad (9\text{-}27)$$

which becomes, by virtue of charge conservation ($z_A + z_B + z_C + \cdots = z_X + z_Y + \cdots$),

$$\log k = \log k^\circ + \frac{(\Delta z^2)^\ddagger A\mu^{1/2}}{1+\mu^{1/2}} \qquad (9\text{-}28)$$

where $(\Delta z^2)^\ddagger = z_X^2 + z_Y^2 - z_A^2 - z_B^2 - z_C^2$. A further illustration of these effects is found in data for the reaction[14] of V^{3+} and VO_2^+, which follows the rate law

$$\frac{-d[V^{3+}]}{dt} = k\frac{[V^{3+}][VO_2^+]}{[H^+]} \qquad (9\text{-}29)$$

The values of k as a function of ionic strength are:

μ/M	0.060	0.20	0.50	1.0	2.0	2.5
k/s^{-1}	16.0	15.3	14.9	15.4	16.9	17.6

We see that k is largely independent of μ. That is consistent with the value of $(\Delta z^2)^\ddagger$ for the net activation process.

$$V^{3+} + VO_2^+ + H_2O \longrightarrow [V_2O_3H_2^{3+}]^\ddagger + H^+ \qquad (\Delta z^2)^\ddagger = 0$$

9-7 SALT EFFECTS AND REACTION MECHANISMS

This section is meant to convey just one point: *The magnitude of the salt effect is a property of the rate law, not of the reaction mechanism.* The classic example[15] of this point is the question whether the urea synthesis from ammonium cyanate is a reaction between the ions NH_4^+ and NCO^- or the neutral molecules NH_3 and HNCO. The distinction proves quite impossible on such a basis.†

The observed salt effect on a rate constant which is a composite of true rate constants and equilibrium constants is the net effect from both sources, the so-called

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†Although considering the bonds which need to be broken and made and the structure of the requisite transition state, one is quite likely to opt for the latter.

"primary salt effect" on the former and the "secondary salt effect" on the latter. (The two have comparable magnitudes and forms, so the terminology may be misleading.)

We shall illustrate the key thesis with one example. Consider the following two mechanisms, schemes I and II, to account for the k_2 rate term of Eq. (9-21).

Scheme I:

$$\mathrm{Fe^{3+} + Cl^- \overset{K_{Fe}}{\rightleftharpoons} FeCl^{2+}} \qquad \Delta Z^2 = -6 \tag{9-30}$$

$$\mathrm{FeCl^{2+} + Sn^{2+} \xrightarrow{k_3} products} \qquad (\Delta Z^2)^{\ddagger} = +8 \tag{9-31}$$

Scheme II:

$$\mathrm{Sn^{2+} + Cl^- \overset{K_{Sn}}{\rightleftharpoons} SnCl^{+}} \qquad \Delta Z^2 = -4 \tag{9-32}$$

$$\mathrm{SnCl^{+} + Fe^{3+} \xrightarrow{k_4} products} \qquad (\Delta Z^2)^{\ddagger} = +6 \tag{9-33}$$

The rate constant k_2, either $k_3 K_{\mathrm{Fe}}$ or $k_4 K_{\mathrm{Sn}}$, has a salt effect which is the same regardless of mechanism. In scheme I, the value of $\log (k_3/k_3^\circ) = 8A\mu^{1/2}/(1 + \mu^{1/2})$, and $\log (K_{\mathrm{Fe}}/K_{\mathrm{Fe}}^\circ) = -6A\mu^{1/2}/(1 + \mu^{1/2})$, whereas the corresponding parameters in scheme II are $\log (k_4/K_4^\circ) = -4A\mu^{1/2}/(1 + \mu^{1/2})$ and $\log (K_{\mathrm{Sn}}/K_{\mathrm{Sn}}^\circ) = 6A\mu^{1/2}/(1 + \mu^{1/2})$; in either case the net effect is $+2A\mu^{1/2}/(1 + \mu^{1/2})$, exactly as shown by Eq. (9-27). Any other mechanism which would lead to the same rate law would be characterized by the same ionic strength dependence. As a consequence, salt effects cannot be invoked as the basis for distinguishing between alternatives consistent with other kinetic data.

9-8 INFLUENCE OF PRESSURE ON SOLUTION REACTIONS

The thermodynamic relation

$$\left(\frac{\partial\, \Delta G^\circ}{\partial P}\right)_T = \Delta V^\circ \tag{9-34}$$

applied to $\Delta G^{\ddagger}$, with $k = (RT/Nh) \exp (-\Delta G^{\ddagger}/RT)$, gives

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = \frac{\partial(-\Delta G^{\ddagger}/RT)}{\partial P} = -\frac{\Delta V^{\ddagger}}{RT} \tag{9-35}$$

and a means of measuring the *volume of activation*. Integration[†] of Eq. (9-35) affords an expression

$$\ln k = \ln k^\circ - \frac{\Delta V^{\ddagger}}{RT} P \tag{9-36}$$

This relation indicates that the rate constant increases with increasing pressure if $\Delta V^{\ddagger}$ is negative (i.e., if the activated complex has a smaller molar volume than the reactants

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[†] The integration is done under the assumption that the volume of activation is independent of pressure. If that is not the case, a further quantity termed the compressibility is introduced to give the expressions:

$$\Delta\beta^{\ddagger} = -d\,\Delta V^{\ddagger}/dP \qquad \ln k = a + bP + cP^2 \qquad \Delta V_0^{\ddagger} = -bRT \qquad \Delta\beta^{\ddagger} = 2cRT$$

together). In practice, pressures of the order of 0.5 to 5 kbar are needed if values are to be meaningful. A plot of ln k versus p is made; it should, according to Eq. (9-36), be linear and have a slope equal to $-\Delta V^{\ddagger}/RT$.

If we consider, for example, a reaction having $\Delta V^{\ddagger} = +5.0\ \mathrm{cm^3\ mol^{-1}}$ at 298 K, a reasonably typical value, the pressure needed to change the rate by a factor of 2 from its value at atmospheric pressure (1 bar = $10^5\ \mathrm{N\ m^{-2}} = 10^5$ Pa = 0.1 MPa) can be calculated as follows:

$$\ln \frac{k_P}{k^\circ} = \ln \frac{1}{2} = \frac{-5.0 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}}}{8.31\ \mathrm{J\ mol^{-1}\ K^{-1}} \times 298\ \mathrm{K}} (P - 10^5)$$

$$P = 10^5 + \frac{\ln 2 \times 8.31 \times 298}{5.0 \times 10^{-6}} = 3.4 \times 10^8\ \mathrm{Pa}$$

which amounts to 3.4×10^3 bar. Even when the volume of activation is relatively large, $\Delta V^{\ddagger} = \pm 40\ \mathrm{cm^3\ mol^{-1}}$, a pressure of 430 bar is needed to cause a factor of 2 change in rate. That stands in contrast to the relatively small variation in temperature needed to effect a comparable change. As a consequence, values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are routinely determined, whereas values of $\Delta V^{\ddagger}$ are much less frequently reported. The special equipment needed to obtain pressures of thousands of atmospheres has limited these studies to a relatively few laboratories. That is unfortunate, because the value of $\Delta V^{\ddagger}$, which represents the change in volume of the reacting system in passing to the transition state, is a meaningful parameter. The corresponding value of $\Delta S^{\ddagger}$ is often given a similar interpretation to infer details of structural changes during the activation step. Yet, volume being a more easily appreciated quantity than entropy, values of $\Delta V^{\ddagger}$ can be of considerable value.

One study[16] useful for illustrative purposes is the thermal decomposition of di-*t*-butyl peroxide. The data given in Table 9-4 are plotted as suggested by Eq. (9-36). The plot of ln k versus P is shown in Fig. 9-3, and the slope, $-1.64 \times 10^{-9}\ \mathrm{m\ s^2\ kg^{-1}}$, gives $\Delta V^{\ddagger} = 5.4\ \mathrm{cm^3\ mol^{-1}}$:

$$\Delta V^{\ddagger} = -\text{slope} \times RT = 1.64 \times 10^{-9}\ \mathrm{m\ s^2\ kg^{-1}} \times \frac{8.314\ \mathrm{kg\ m^2\ s^{-2}}}{\mathrm{mol\ K}} \times 393\ \mathrm{K}$$

$$= 5.4 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}} = 5.4\ \mathrm{cm^3\ mol^{-1}}$$

The positive value of $\Delta V^{\ddagger}$ is consistent with a mechanism in which a dissociative rate-limiting step is proposed. As in the study of temperature dependences, one must

Table 9-4 Pressure dependence of the rate constant for the thermal decomposition of Di-*t*-butyl peroxide[a]

P/MPa	$10^6\ k/\mathrm{s^{-1}}$	P/MPa	$10^6\ k/\mathrm{s^{-1}}$
0.1	13.4	448	6.6
204	9.5	527	5.7
290	8.0		

[a] In toluene at 120°C. Data from Ref. 16.

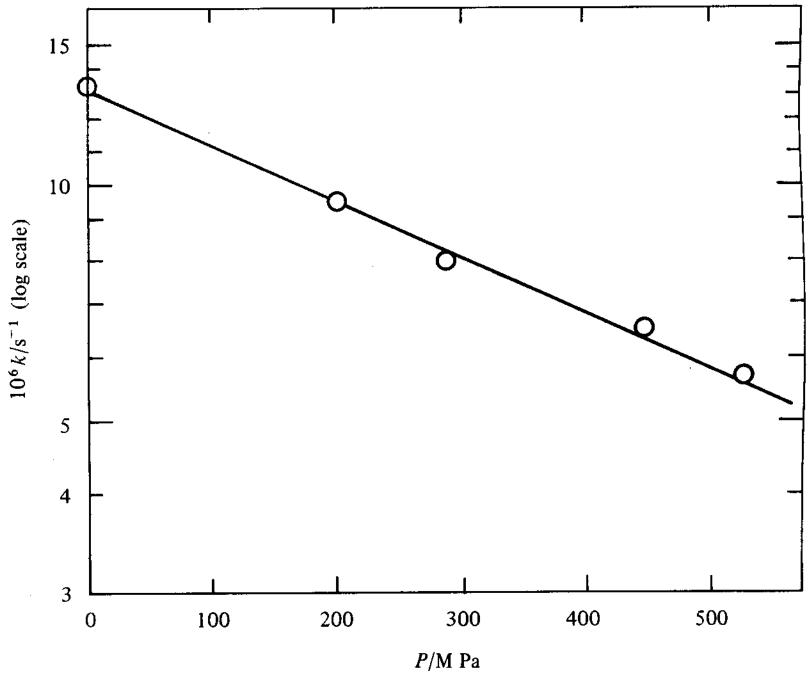

Figure 9-3. A plot of ln k versus P for the thermal decomposition of di-*t*-butyl peroxide in toluene at 120°C. Data from Table 9-4 and Ref. 16.

be aware that the experimental rate constant will represent a composite of two or more rate constants if the mechanism is at all complex. In such a case the plot of ln k versus P may not be linear, and for the same reason ln k versus $1/T$ will not be. Moreover, considering the values of $\Delta V^{\ddagger}$ in a series of compounds, one recognizes that the relative importance of the rate constants in the composite may differ, so that comparisons must be made with caution.

9-9 CONCENTRATION UNITS IN SOLUTION REACTIONS

The value of $\Delta S^{\ddagger}$ is dependent upon the choice of concentration units for the rate constant; the latter is equivalent to the choice of standard state.

Consider just one case. If a particular second-order rate constant is expressed in the customary units M^{-1} s^{-1} (dm^3 mol^{-1} s^{-1}) and has $\Delta S^{\ddagger} = -21.0$ J mol^{-1} K^{-1}, then factors of $R \ln 10^3$ must be introduced if the concentration scale is changed to a volume different from 1 dm^3 by a factor 10^3. If the units dm^3 $mmol^{-1}$ s^{-1} are used, $\Delta S^{\ddagger} = -21.0 - R \ln 10^3 = -78.4$ J mol^{-1} K^{-1}. Units cm^3 mol^{-1} s^{-1} for k would give $\Delta S^{\ddagger} = -21.0 + R \ln 10^3 = 36.4$ J mol^{-1} K^{-1}. Clearly the inherent value or sign of $\Delta S^{\ddagger}$ is of no intrinsic importance unless the reference state is kept in mind and comparison reactions are expressed on the same basis.

A similar statement has already been made about a second-order gas-phase reaction in Sec. 6-2. First-order reactions are not influenced; for other cases the effect depends upon the order of the reaction. Comparisons of the magnitude or sign $\Delta S^{\ddagger}$ values for reactions of different kinetic orders is clearly unjustified.

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PROBLEMS

9-1 *Solvent effects.* Equation (9-13) contains the factor $(\epsilon - 1)/(2\epsilon + 1)$.

(*a*) Show that the factor may be expanded as

$$\frac{\epsilon - 1}{2\epsilon + 1} = \frac{1}{2} - \frac{3}{4\epsilon} + \frac{3}{8\epsilon^2} - \frac{3}{16\epsilon^3} + \cdots$$

(*b*) Find the range of dielectric constants over which the first two terms of the expansion hold to within 1 percent; to within 10%.

(*c*) Show that in the range of (*b*) the rate constant depends upon dielectric constant according to

$$\ln \frac{k_{\text{actual}}}{k_\infty} = \frac{3N}{4\epsilon RT}\left[\frac{A^2}{r_A{}^3} + \frac{B^2}{r_B{}^3} - \frac{\ddagger^2}{r_\ddagger{}^3}\right]$$

where k_∞ represents the rate constant in a medium of infinite dielectric constant. Test this expression by a plot of $\ln k$ versus $1/\epsilon$ using data in Table 9-1 for the reaction of Eq. (9-2).

9-2 *Salt effects.* Rosseinsky [*J. Inorg. Nucl. Chem.*, 33:3976 (1971)] pointed out that the rate of reaction of vanadium(V) with iodide ions is independent of ionic strength. The rate law is

$-d[\mathrm{V(V)}]/dt = k[\mathrm{V(V)}][\mathrm{I}^-][\mathrm{H}^+]^2$. What is the charge on the predominant V(V) species in these solutions?

9-3 *Salt effects.* Postmus and King [*J. Phys. Chem.*, 59:1216 (1955)] found that the reaction $\mathrm{Cr}^{3+} + \mathrm{NCS}^- = \mathrm{CrNCS}^{2+}$ follows this rate expression in the forward direction:

$$\frac{d[\mathrm{CrNCS}^{2+}]}{dt} = (k_1 + k_2[\mathrm{H}^+]^{-1})[\mathrm{Cr}^{3+}][\mathrm{NCS}^-]$$

At 25°C and $\mu = 0.070$ M, $k_1 = 4.28 \times 10^{-6}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ and $k_2 = 1.96 \times 10^{-8}\ \mathrm{s}^{-1}$. Estimate k_1 and k_2 at $\mu = 0.010$ M.

9-4 *Salt effects.* Seel and Winkler found that the decomposition of *N*-hydroxylamine-*N*-sulfonate ($=\mathrm{X}^{2-}$) follows a rate law $-d[\mathrm{X}^{2-}]/dt = k[\mathrm{X}^{2-}][\mathrm{H}^+]$. The slope of log k versus $0.509\ \mu^{1/2}$, in a series of experiments at pH 7.00, has a slope −3.0. Reconcile that result with Eq. (9-20). (Remember that $\mathrm{pH} = -\log a_{\mathrm{H}^+}$.)

9-5 *Volume of activation.* The rate constant for the base hydrolysis of $\mathrm{ClC(CH_3)_2C{\equiv}CH}$ [LeNoble, Tatsukami, and Morris, *J. Am. Chem. Soc.*, 92:5681 (1970)] varies with pH as shown below. Compute $\Delta V^{\ddagger}$.

p/kbar	0.001	1.055	3.023	5.062
$10^6\ k_{298}/\mathrm{M}^{-1}\ \mathrm{s}^{-1}$	2.68	2.38	1.55	1.20

9-6 *Volume of activation.* Swaddle [*Inorg. Chem.*, 15:2644 (1976)] gives the following values for the rate of exchange of *trans*-$\mathrm{Co(en)_2(H_2{}^{18}O)_2}^{3+}$ and solvent at 308 K. Calculate $\Delta V^{\ddagger}$. What is the implication of that value for the mechanism?

p/MPa	0.1	6.4	102.5	152.4	201.3	250.0	301.9
$10^5\ k_{\mathrm{ex}}/\mathrm{s}^{-1}$	6.29	6.27	5.05	4.23	4.17	3.52	3.16

Note: 0.1 MPa (megapascal) = 1 bar.